

PAT-NO: JP410089056A
DOCUMENT- JP 10089056 A
IDENTIFIER:
TITLE: EXHAUST EMISSION CONTROL CATALYST FOR DIESEL
ENGINE

PUBN-DATE: April 7, 1998

INVENTOR-INFORMATION:

NAME	COUNTRY
TAGUCHI, MICHIO	

ASSIGNEE-INFORMATION:

NAME	COUNTRY
TOYOTA MOTOR CORP N/A	

APPL-NO: JP08244799

APPL-DATE: September 17, 1996

INT-CL F01N003/28 , F01N003/28 , B01D053/86 , B01D053/94 ,
(IPC): B01J035/04 , B01J035/04

ABSTRACT:

PROBLEM TO BE SOLVED: To control HC and SOF in a low temperature range of exhaust gas, and also suppress formation of sulfate in a high temperature range thereof, by increasing a linear velocity of exhaust gas on an exhaust gas outlet side higher than a linear velocity of exhaust gas on an exhaust gas inlet side.

SOLUTION: An exhaust emission control catalyst is formed into a circular cone shape and many honeycomb passages 1 are arranged in the catalyst, so that a linear velocity of exhaust gas on the exhaust gas outlet side of the exhaust emission control catalyst is increased higher than a linear velocity of exhaust gas on the exhaust gas inlet side thereof. Hereby, the linear velocity of exhaust gas on the exhaust gas inlet side is decreased, contact time between exhaust gas and the catalyst is secured, and HC and SOF can be controlled from

the low temperature range of exhaust gas to the high temperature range thereof. As the kind of the catalyst, a honeycomb catalyst in which a carrying layer such as aluminum is formed in a honeycomb carrying case material formed of heat-proof ceramics such as cordierite or metallic foil, and so on, and catalytic noble metals such as rhodium and palladium is carried in the carrying layer, or a pellet catalyst in which the catalytic noble metals are carried in pellet such as amunina, can be exemplified.

COPYRIGHT: (C)1998,JPO

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-089056

(43)Date of publication of application : 07.04.1998

(51)Int.Cl.

F01N 3/28
F01N 3/28
B01D 53/86
B01D 53/94
B01J 35/04
B01J 35/04

(21)Application number : 08-244799

(71)Applicant : TOYOTA MOTOR CORP

(22)Date of filing : 17.09.1996

(72)Inventor : TAGUCHI MICHIO

(54) EXHAUST EMISSION CONTROL CATALYST FOR DIESEL ENGINE

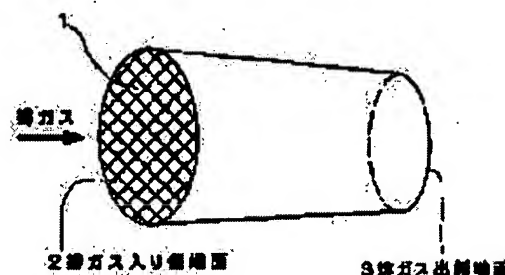
(57)Abstract:

PROBLEM TO BE SOLVED: To control HC and SOF in a low temperature range of exhaust gas, and also suppress formation of sulfate in a high temperature range thereof, by increasing a linear velocity of exhaust gas on an exhaust gas outlet side higher than a linear velocity of exhaust gas on an exhaust gas inlet side.

SOLUTION: An exhaust emission control catalyst is formed into a circular cone shape and many honeycomb passages 1 are arranged in the catalyst, so that a linear velocity of exhaust gas on the exhaust gas outlet side of the exhaust emission control catalyst is increased higher than a linear velocity of exhaust gas on the exhaust gas inlet side thereof. Hereby, the linear velocity of exhaust gas on the exhaust gas inlet side is decreased, contact time

between exhaust gas and the catalyst is secured, and HC and SOF can be controlled from the low temperature range of exhaust gas to

the high temperature range thereof. As the kind of the catalyst, a honeycomb catalyst in which a carrying layer such as aluminum is formed in a honeycomb carrying case material formed of heat-proof ceramics such as cordierite or metallic foil, and so on, and catalytic noble metals such as rhodium and palladium is carried in the carrying layer, or a pellet catalyst in which the catalytic noble metals are carried in pellet such as amunina, can be exemplified.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the catalyst for emission gas purification for DE which reduces the discharge of a diesel particulate while carrying out oxidization purification of HC (hydrocarbon) and SOF (Soluble Organic Fraction) which are contained in the exhaust gas of a diesel power plant (it is called Following DE).

[0002]

[Description of the Prior Art] About the gasoline engine, the harmful matter in exhaust gas is decreasing in number certainly by advance of the technique in which severe regulation and severe it of exhaust gas can be coped with. However, about DE, technical development is also behind also in regulation from the unique situation that an injurious ingredient is discharged mainly as a particulate, compared with the gasoline engine, and development of the emission-gas-purification catalyst which can be purified certainly is desired from it.

[0003] As a DE exhaust gas purge currently developed by current, it roughly divides and the approach (have no catalyst with a catalyst) using a trap and the open-type SOF decomposition catalyst are known. Among these, the approach using a trap catches a diesel particulate, regulates the discharge, and is effective in exhaust gas especially with the high ratio of a dry suit. However, by the approach using a trap, the regeneration equipment for incinerating the caught diesel particulate was needed, and it has left many technical problems practically -- the lock out or system by the crack of the catalyst structure at the time of playback and the ash becomes complicated.

[0004] On the other hand, as shown in JP,3-38255,A, the catalyst which supported catalyst metals, such as a platinum metal, is used for support layers, such as an activated alumina, as well as a gasoline engine, and with CO and HC, an open-type SOF decomposition catalyst carries out oxidative degradation of the SOF, and is purifying it. Although there is a fault that this open-type SOF decomposition catalyst has the low elimination factor of a dry suit, since the amount of a dry suit has the big merit that regeneration equipment is unnecessary, possible [decreasing by amelioration of DE or the fuel itself], improvement in one step of future technique is expected.

[0005] however, an open-type SOF decomposition catalyst -- setting -- a pyrosphere -- SO₂ in exhaust gas up to -- it oxidizes -- having -- SO₃ SO₄ It generates and there is a problem that become sulfate and a particulate amount increases conversely. This is SO₂. Although not measured as a particulate, sulfate is because it is measured as a particulate. Especially in DE, oxygen gas exists mostly in exhaust gas, and it is SO₂. It is easy to produce oxidation reaction.

[0006] So, the exhaust gas purge which controls the emission close area of a catalyst based on exhaust gas temperature is indicated by JP,5-302510,A. According to this exhaust gas purge, when exhaust gas temperature exceeds predetermined temperature, it controls so that the emission close area of a catalyst becomes small. Since the rate of flow of the exhaust gas which passes a catalyst by this increases, the contact time of exhaust gas and a catalyst becomes short, and it is SO₂. Oxidation is controlled.

[0007]

[Problem(s) to be Solved by the Invention] By the way, oxidation reaction of HC or SOF is SO₂ although comparatively generated from a low-temperature region to a pyrosphere. It is not generated but oxidation reaction is produced only in a pyrosphere in a low-temperature region. Moreover, the oxidation reaction rate of the oxidized component in exhaust gas changes with classes of oxidized component, and is SO₂. The oxidation reaction rate of HC and SOF is larger than an oxidation reaction rate.

[0008] Therefore, in the pyrosphere of exhaust gas, when the concentration of HC and SOF is high, HC and SOF oxidize preferentially, and it is SO₂. Since it is hard to produce oxidation reaction, generation of sulfate is controlled. However, it is SO₂ when the concentration of HC and SOF becomes low. Oxidation will arise and

sulfate will generate. Therefore, since the concentration of HC and SOF is high in an entering [a catalyst]-exhaust gas side in the pyrosphere of exhaust gas, it is SO₂. Although it is hard to produce oxidation, since the concentration of HC and SOF is low in the exhaust gas appearance side, it is SO₂. Oxidation arises and there is a problem that sulfate generates.

[0009] Therefore, though the rate of flow of exhaust gas is increased using the approach indicated by JP,5-302510,A, in the pyrosphere of exhaust gas, it sets to the exhaust gas appearance side of a catalyst, and it is SO₂. It is difficult for oxidation to arise and to control generation of sulfate greatly. Moreover, back SO₂ to which HC and SOF oxidized when shortening the overall length of a catalyst Exhaust gas can be discharged before oxidation arises. However, when the overall length of a catalyst is shortened and exhaust gas temperature is a low-temperature region, before oxidation of HC and SOF fully arises, exhaust gas will be discharged, and the purification engine performance of HC and SOF comes to run short of.

[0010] This invention is made in view of such a situation, HC and SOF can fully be purified in the low-temperature region of exhaust gas, and it aims at offering the catalyst for emission gas purification which can control generation of sulfate greatly in a pyrosphere.

[0011]

[Means for Solving the Problem] The description of the catalyst for emission gas purification according to claim 1 for DE which solves the above-mentioned technical problem is to have made linear velocity of the exhaust gas by the side of exhaust gas appearance larger than the linear velocity of the exhaust gas by the side of entering exhaust gas. Moreover, the description of the catalyst for emission gas purification according to claim 2 for DE is in the catalyst for emission gas purification according to claim 1 to have made small the cross section by the side of exhaust gas appearance to the entering-exhaust gas side, and have made into 20 - 50% cross-section percentage reduction expressed with $\{100 \times (\text{entering side cross-section-appearance side cross section}) / \text{entering side cross section}\}$.

[0012]

[Embodiment of the Invention] With the catalyst for emission gas purification of this invention, linear velocity of the exhaust gas by the side of exhaust gas appearance is made larger than the linear velocity of the exhaust gas by the side of entering exhaust gas. Therefore, since the linear velocity of exhaust gas is small in an entering-exhaust gas side, the contact time of exhaust gas and a catalyst can be secured and HC and SOF are purified from the low-temperature region of exhaust gas to a pyrosphere.

[0013] On the other hand, in an exhaust gas appearance side, since the linear velocity of exhaust gas is large, the contact time of exhaust gas and a catalyst becomes short. Therefore, SO₂ in the pyrosphere of exhaust gas It is hard coming to generate oxidation reaction, and generation of sulfate is controlled greatly. In addition, linear velocity means the rate of flow of the exhaust gas which passes the unit area of a catalyst cross section. In order to make linear velocity of the exhaust gas by the side of exhaust gas appearance larger than the linear velocity of the exhaust gas by the side of entering exhaust gas, making small the cross section by the side of exhaust gas appearance to an entering-exhaust gas side as one means is mentioned. If it does in this way, since the cross section of a catalyst is large, in an entering-exhaust gas side, the linear velocity of exhaust gas is small.

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The description of the catalyst for emission gas purification according to claim 1 for DE which solves the above-mentioned technical problem is to have made linear velocity of the exhaust gas by the side of exhaust gas appearance larger than the linear velocity of the exhaust gas by the side of entering exhaust gas. Moreover, the description of the catalyst for emission gas purification according to claim 2 for DE is in the catalyst for emission gas purification according to claim 1 to have made small the cross section by the side of exhaust gas appearance to the entering-exhaust gas side, and have made into 20 - 50% cross-section percentage reduction expressed with $\{100 \times (\text{entering side cross-section-appearance side cross section}) / \text{entering side cross section}\}$.

[0012]

[Embodiment of the Invention] With the catalyst for emission gas purification of this invention, linear velocity of the exhaust gas by the side of exhaust gas appearance is made larger than the linear velocity of the exhaust gas by the side of entering exhaust gas. Therefore, since the linear velocity of exhaust gas is small in an entering-exhaust gas side, the contact time of exhaust gas and a catalyst can be secured and HC and SOF are purified from the low-temperature region of exhaust gas to a pyrosphere.

[0013] On the other hand, in an exhaust gas appearance side, since the linear velocity of exhaust gas is large, the contact time of exhaust gas and a catalyst becomes short. Therefore, SO₂ in the pyrosphere of exhaust gas It is hard coming to generate oxidation reaction, and generation of sulfate is controlled greatly. In addition, linear velocity means the rate of flow of the exhaust gas which passes the unit area of a catalyst cross section. In order to make linear velocity of the exhaust gas by the side of exhaust gas appearance larger than the linear velocity of the exhaust gas by the side of entering exhaust gas, making small the cross section by the side of exhaust gas appearance to an entering-exhaust gas side as one means is mentioned. If it does in this way, since the cross section of a catalyst is large, in an entering-exhaust gas side, the linear velocity of exhaust gas is small. However, in an exhaust gas appearance side, since the exhaust gas of the same volume as an entering-exhaust gas side flows into the place where the cross section is small, and the exhaust gas of the volume enters and it is discharged at the same rate as a gas side, the linear velocity of exhaust gas increases.

[0014] Thus, in order to change the cross section by the entering-exhaust gas and exhaust gas appearance side, a catalyst is entered, it is good also as a taper configuration to which the cross section becomes small gradually continuously from a gas side, and the cross section can become small at the shape of a phase. Moreover, it is good also as such a configuration with one catalyst, and two or more catalysts from which a path differs can be connected, and it can also consider as such a configuration.

[0015] Moreover, as a means which enlarges linear velocity of the exhaust gas by the side of exhaust gas appearance, other force, such as a centrifugal force, can be used and linear velocity by the side of exhaust gas appearance can also be mechanically made larger [than the linear velocity of the exhaust gas by the side of entering exhaust gas] than an entering side. However, since equipment will become large-scale and fault arises in respect of a tooth space and cost, especially a means to change the cross section of a catalyst as mentioned above is desirable.

[0016] When adopting the means which makes small the cross section by the side of exhaust gas appearance to an entering-exhaust gas side, it is desirable to make into 20 - 50% cross-section percentage reduction expressed with $\{100 \times (\text{entering side cross-section-appearance side cross section}) / \text{entering side cross section}\}$. The rate of increase of linear velocity becomes 25% or less, if cross-section percentage reduction is lower than 20%, the effectiveness which carried out the configuration in this way will be small, and it will set to the pyrosphere of exhaust gas, and it is SO₂. It becomes difficult for oxidation to arise and to control generation of sulfate. Moreover, if cross-section percentage reduction becomes higher than 50%, it will become difficult to oxidize HC and SOF which remained

without being an entering-exhaust gas side and oxidizing by the exhaust gas appearance side, and the rate of purification of HC and SOF will fall.

[0017] Support layers, such as an alumina, are formed in the honeycomb support base material formed from the heat-resistant ceramics or metallic foils, such as cordierite, etc. as a class of catalyst, and the pellet catalyst which supported catalyst noble metals on pellets, such as a honeycomb catalyst which supported catalyst noble metals, such as platinum, a rhodium, and palladium, to it, or an alumina, is illustrated.

[0018] What is necessary is for what is necessary to be just to form the configuration of a honeycomb support base material such in the case of a honeycomb catalyst, and just to fill up the case of such a configuration with a pellet catalyst in the case of a pellet catalyst, in order to change the cross section by the entering-exhaust gas and exhaust gas appearance side.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

(Example 1) The catalyst for emission gas purification of this example is shown in drawing 1 . This catalyst has the honeycomb path 1 of a large number prolonged in nothing and shaft orientations in a truncated-cone configuration. And the diameter of the end face 3 by the side of 117mm and exhaust gas appearance is [the diameter of the end face 2 by the side of entering exhaust gas] 82mm.

[0020] Hereafter, the manufacture approach of this catalyst is explained and it replaces with detailed explanation of a configuration. By extrusion molding, the cylinder-like honeycomb object was first formed from cordierite. And press forming of the honeycomb object was carried out before desiccation, it considered as the truncated-cone configuration, desiccation baking of it was carried out, and the diameter of an end side formed the honeycomb support base material of the truncated-cone configuration 82mm and whose die length the diameter of 117mm and an other end side is 122mm and volume of 898 cc.

[0021] Next, the slurry which mixed alumina sol was prepared for alpha-alumina, the honeycomb support base material was pulled up after being immersed, the excessive slurry was wiped and paid, it calcinated at 500 degrees C after 60-hour desiccation by 120 degrees C for 1 hour, and the alumina coat layer was formed. The amount of coats of an alumina coat layer is 100g per 1l. of honeycomb support base materials. Furthermore, after having been immersed into the dinitrodiammine platinum solution of predetermined concentration, pulling up the honeycomb support base material with an alumina coat layer and blowing off excessive waterdrop, it heat-treated at 250 degrees C for 1 hour, platinum was supported, and it considered as the catalyst of this example. The amount of support of platinum is 2g per 1l. of honeycomb support base materials.

[0022] The exhaust air system of the diesel power plant of 2.6L was equipped with this catalyst so that the end face of the larger one with a diameter of 117mm might turn into a side edge side containing exhaust gas, and evaluation on an engine bench was performed. After circulating 500-degree C exhaust gas for a catalyst in engine-speed 2000rpm for 1 hour, the temperature of exhaust gas is lowered and it sets at 400 degrees C, 300 degrees C, and 200 degrees C, and evaluation is the rate of purification and SO₂ of HC. The invert ratio was measured. The measurement in each temperature takes for 10 minutes, respectively, was reduced to the temperature, and after holding at the temperature further for 1 hour, it was measured. A result is shown in drawing 3 . In addition, SO₂ SO₂ which decreased on the catalyst to entering gas with the invert ratio A rate is said and it is equivalent to the amount of generation of sulfate.

[0023] (Example 2) The catalyst of this example is shown in drawing 2 . This catalyst consists of the 1st honeycomb catalyst 4 of the shape of a cylinder with a diameter [of 117mm], and a die length of 61mm, and the 2nd honeycomb catalyst 5 of the shape of a cylinder with a diameter [of 82mm], and a die length of 61mm, and the 1st honeycomb catalyst 4 and the 2nd honeycomb catalyst 5 are arranged in the case 6 made from stainless steel at the serial. In addition, the 1st honeycomb catalyst 4 and the 2nd honeycomb catalyst 5 were manufactured like the catalyst of an example 1, respectively.

[0024] The exhaust air system of the diesel power plant of 2.6L was equipped with this catalyst so that the 1st honeycomb catalyst 4 side might become an entering-exhaust gas side, and the rate of purification of HC and the invert ratio of SO₂ were measured like the example 1. A result is shown in drawing 3 and drawing 4 .

(Example 3) The catalyst of this example is the same as that of an example 2 except having used the 2nd honeycomb catalyst 5 with a diameter [of 111mm], and a die length of 61mm. It is the rate of purification and SO₂ of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 4 .

[0025] (Example 4) The catalyst of this example is the same as that of an example 2 except having used the 2nd honeycomb catalyst 5 with a diameter [of 105mm], and a die length of 61mm. It is the rate of purification and SO₂

of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 4 .

(Example 5) The catalyst of this example is the same as that of an example 2 except having used the 2nd honeycomb catalyst 5 with a diameter [of 74mm], and a die length of 61mm. It is the rate of purification and SO₂ of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 4 .

[0026] (Example 6) The catalyst of this example is the same as that of an example 2 except having used the 2nd honeycomb catalyst 5 with a diameter [of 95mm], and a die length of 61mm. It is the rate of purification and SO₂ of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 4 .

(Example 1 of a comparison) The honeycomb catalyst was formed like the example 1 using the honeycomb support base material of the shape of a cylinder with a diameter [of 117mm], and a die length of 122mm. It is the rate of purification and SO₂ of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 3 and drawing 4 .

[0027] (Example 2 of a comparison) The honeycomb catalyst was formed like the example 1 using the honeycomb support base material of the shape of a cylinder with a diameter [of 82mm], and a die length of 122mm. It is the rate of purification and SO₂ of HC like [catalyst / this] an example 1. An invert ratio is measured and a result is shown in drawing 3 .

(Evaluation) It is SO [in / from drawing 3 / in especially the catalyst of the example 1 of a comparison / a pyrosphere]2. Although an invert ratio is higher than others, since the linear velocity of exhaust gas is small, this is SO₂ at an exhaust gas appearance side especially with little HC concentration to the exhaust gas appearance side from an entering-exhaust gas side. It is because oxidation arose. Moreover, although especially the catalyst of the example 2 of a comparison has a rate of HC purification lower than others in a low-temperature region, this is because HC which did not oxidize was discharged from the entering-exhaust gas side at the exhaust gas appearance side since the linear velocity of exhaust gas was large.

[0028] On the other hand, it compares with the example 1 of a comparison, and the example 2 of a comparison, and the catalyst of an example 1 and an example 2 is a high rate of HC purification, and low SO₂. The invert ratio is shown. It is clear that its it is the effectiveness which made small the cross section by the side of exhaust gas appearance while this enlarges the cross section by the side of entering exhaust gas. Moreover, the rate of HC purification and SO₂ in 300 degrees C of drawing 4 to each catalyst An invert ratio is read and the result of having arranged it by the cross-section percentage reduction of each catalyst is shown in drawing 5 .

[0029]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the perspective view of the catalyst for emission gas purification of one example of this invention.

[Drawing 2] It is the sectional view of the catalyst for emission gas purification of the 2nd example of this invention.

[Drawing 3] Entering gas temperature, the rate of HC purification, and SO₂ It is the graph which shows relation with an invert ratio.

[Drawing 4] Entering gas temperature, the rate of HC purification, and SO₂ It is the graph which shows relation with an invert ratio.

[Drawing 5] Cross-section percentage reduction, the rate of HC purification, and SO₂ It is the graph which shows relation with an invert ratio.

[Description of Notations]

1: Honeycomb path 2: Side edge side containing exhaust gas 3: Exhaust gas appearance side edge side
4: The 1st honeycomb catalyst 5: The 2nd honeycomb catalyst 6: Case

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The catalyst for emission gas purification for diesel power plants characterized by making linear velocity of the exhaust gas by the side of exhaust gas appearance larger than the linear velocity of the exhaust gas by the side of entering exhaust gas.

[Claim 2] The catalyst for emission gas purification according to claim 1 for diesel power plants characterized by having made small the cross section by the side of exhaust gas appearance to the entering-exhaust gas side, and making into 20 - 50% cross-section percentage reduction expressed with $\{100 \times (\text{entering side cross-section-appearance side cross section}) / \text{entering side cross section}\}$.

[Translation done.]

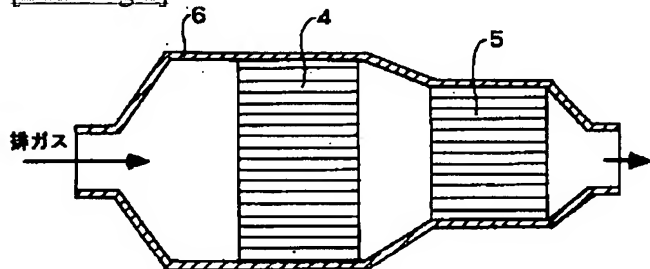
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

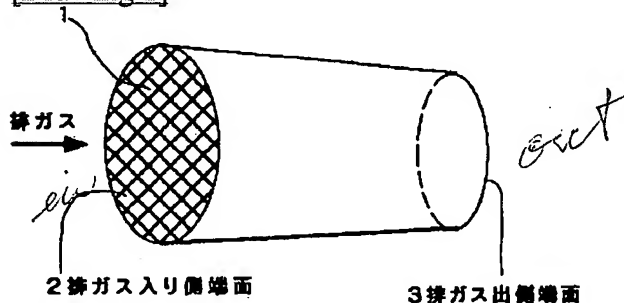
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

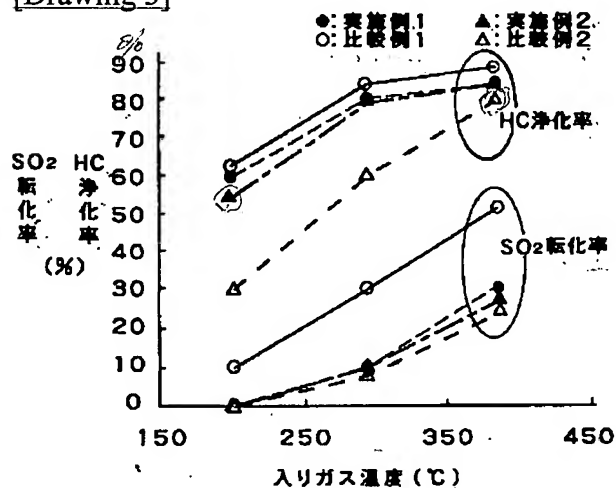
[Drawing 2]



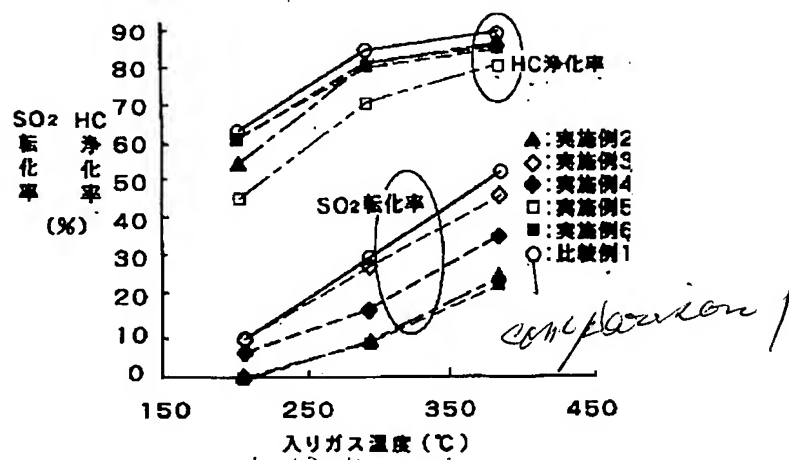
[Drawing 1]



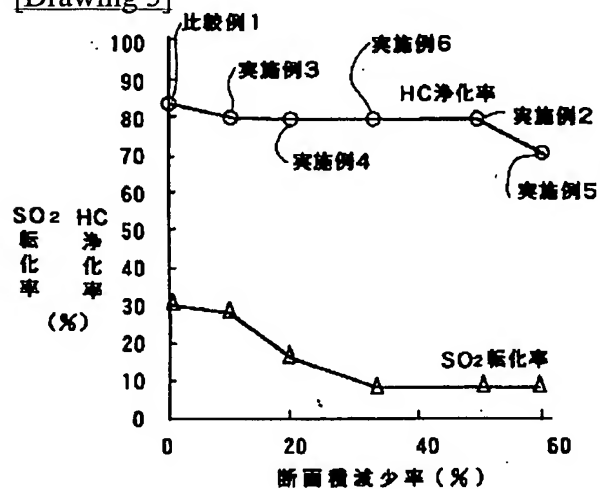
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]

(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平10-89056

(43)公開日 平成10年(1998)4月7日

(51)Int.Cl. ⁶	識別記号	FI		
F01N 3/28	301	F01N 3/28	301P	
			301W	
	ZAB		ZAB	
B01D 53/86	ZAB	B01J 35/04	ZAB	
53/94			301K	
審査請求 未請求 請求項の数2 OL (全5頁) 最終頁に続く				

(21)出願番号 特願平8-244799

(22)出願日 平成8年(1996)9月17日

(71)出願人 000003207

トヨタ自動車株式会社

愛知県豊田市トヨタ町1番地

(72)発明者 田口 教夫

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

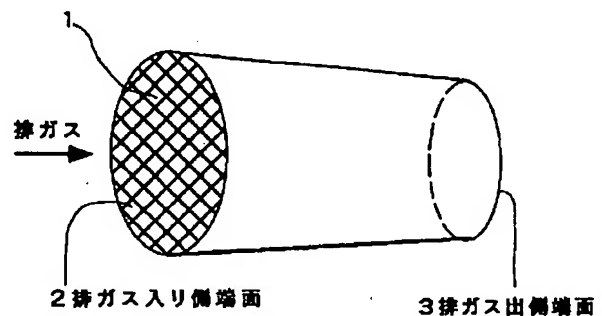
(74)代理人 弁理士 大川 宏

(54)【発明の名称】 ディーゼルエンジン用排ガス浄化用触媒

(57)【要約】

【課題】排ガスの低温域においてHC及びSOFを十分に浄化でき、高温域においてはサルフェートの生成を大きく抑制できる排ガス浄化用触媒を提供する。

【解決手段】排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくする。排ガス出側では排ガスの線速度が大きいため、排ガスと触媒との接触時間が短くなり、排ガスの高温域におけるSO₂の酸化反応が生じにくくなって、サルフェートの生成が抑制される。



【特許請求の範囲】

【請求項1】 排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくしたことを特徴とするディーゼルエンジン用排ガス浄化用触媒。

【請求項2】 排ガス入り側に対し排ガス出側の断面積を小さくし、 $\{100 \times (\text{入り側断面積} - \text{出側断面積}) / \text{入り側断面積}\}$ で表される断面積減少率を20～50%としたことを特徴とする請求項1記載のディーゼルエンジン用排ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ディーゼルエンジン（以下DEという）の排ガス中に含まれるHC（炭化水素）及びSOF（Soluble Organic Fraction）を酸化浄化するとともに、ディーゼルパティキュレート（ディーゼル微粒子）の排出量を低減するDE用排ガス浄化用触媒に関する。

【0002】

【従来の技術】ガソリンエンジンについては、排ガスの厳しい規制とそれに対処できる技術の進歩により、排ガス中の有害物質は確実に減少している。しかしDEについては、有害成分が主としてパティキュレートとして排出されるという特異な事情から、規制も技術の開発もガソリンエンジンに比べて遅れており、確実に浄化できる排ガス浄化触媒の開発が望まれている。

【0003】現在までに開発されているDE排気ガス浄化装置としては、大きく分けてトラップを用いる方法（触媒無しと触媒付き）と、オープン型SOF分解触媒とが知られている。このうちトラップを用いる方法は、ディーゼルパティキュレートを捕捉してその排出を規制するものであり、特にドライスツートの比率の高い排気ガスに有効である。しかしながらトラップを用いる方法では、捕捉されたディーゼルパティキュレートを焼却するための再生処理装置が必要となり、再生時の触媒構造体の割れ、アッシュによる閉塞あるいはシステムが複雑になるなど、実用上多くの課題を残している。

【0004】一方オープン型SOF分解触媒は、例えば特開平3-38255号公報に示されるように、ガソリンエンジンと同様に活性アルミナなどの担持層に白金族金属などの触媒金属を担持した触媒が利用され、COやHCとともにSOFを酸化分解して浄化している。このオープン型SOF分解触媒は、ドライスツートの除去率が低いという欠点があるが、ドライスツートの量はDEや燃料自体の改良によって低減することが可能であり、かつ再生処理装置が不要という大きなメリットがあるため、今後の一段の技術の向上が期待されている。

【0005】ところがオープン型SOF分解触媒においては、高温域で排ガス中のSO₂までも酸化されてSO₃やSO₄が生成し、サルフェートとなって逆にパティキュレート量が増大するという問題がある。これは、SO₂はパティキュレートとして測定されないが、サルフェートはパティキュレートとして測定されるためである。

特にDEにおいては排ガス中に酸素ガスが多く存在し、SO₂の酸化反応が生じやすい。

【0006】そこで特開平5-302510号公報には、排ガス温度に基づいて触媒の排ガス流入面積を制御する排ガス浄化装置が開示されている。この排ガス浄化装置によれば、排ガス温度が所定温度を超えた場合に、触媒の排ガス流入面積が小さくなるように制御する。これにより触媒を通過する排ガスの流速が増大するため、排ガスと触媒との接触時間が短くなり、SO₂の酸化が抑制される。

【0007】

【発明が解決しようとする課題】ところで、HCやSOFの酸化反応は比較的低温域から高温域まで生じるが、SO₂の酸化反応は低温域では生じず高温域でのみ生じる。また、排ガス中の被酸化成分の酸化反応速度は被酸化成分の種類によって異なり、SO₂の酸化反応速度よりHC及びSOFの酸化反応速度の方が大きい。

【0008】したがって排ガスの高温域において、HC及びSOFの濃度が高い場合には、HC及びSOFが優先的に酸化され、SO₂の酸化反応は生じにくい。しかしHC及びSOFの濃度が低くなると、SO₂の酸化が生じサルフェートが生成してしまう。そのため排ガスの高温域においては、触媒の排ガス入り側ではHC及びSOFの濃度が高いためSO₂の酸化が生じにくい。排ガス出側ではHC及びSOFの濃度が低くなっているためにSO₂の酸化が生じ、サルフェートが生成するという問題がある。

【0009】したがって、特開平5-302510号公報に開示された方法を用いて排ガスの流速を増大させたとしても、排ガスの高温域では触媒の排ガス出側においてSO₂の酸化が生じ、サルフェートの生成を大きく抑制することは困難である。また、触媒の全長を短くすれば、HC及びSOFが酸化された後SO₂の酸化が生じる前に排ガスを排出することができる。しかし触媒の全長を短くすると、排ガス温度が低温域の場合に、HC及びSOFの酸化が十分に生じないうちに排ガスが排出されることとなり、HC及びSOFの浄化性能に不足するようになる。

【0010】本発明はこのような事情に鑑みてなされたものであり、排ガスの低温域においてHC及びSOFを十分に浄化でき、高温域においてはサルフェートの生成を大きく抑制できる排ガス浄化用触媒を提供することを目的とする。

【0011】

【課題を解決するための手段】上記課題を解決する請求項1に記載のDE用排ガス浄化用触媒の特徴は、排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくしたことにある。また請求項2に記載のDE用排ガス浄化用触媒の特徴は、請求項1に記載の排ガス

浄化用触媒において、排ガス入り側に対し排ガス出側の断面積を小さくし、 $\{100 \times (\text{入り側断面積} - \text{出側断面積}) / \text{入り側断面積}\}$ で表される断面積減少率を20～50%としたことにある。

【0012】

【発明の実施の形態】本発明の排ガス浄化用触媒では、排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくしている。したがって、排ガス入り側では排ガスの線速度が小さいので、排ガスと触媒との接触時間を確保でき、排ガスの低温域から高温域までHC及びSO_Fが浄化される。

【0013】一方、排ガス出側では、排ガスの線速度が大きいため、排ガスと触媒との接触時間が短くなる。したがって、排ガスの高温域におけるSO₂の酸化反応が生じにくくなり、サルフェートの生成が大きく抑制される。なお、線速度とは、触媒断面の単位面積を通過する排ガスの流速をいう。排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくするには、一つの手段として、排ガス入り側に対し排ガス出側の断面積を小さくすることが挙げられる。このようにすれば、排ガス入り側では触媒の断面積が大きいため排ガスの線速度が小さい。しかし排ガス出側では、断面積が小さいところに排ガス入り側と同じ体積の排ガスが流入し、またその体積の排ガスが入りガス側と同じ速度で排出されるため、排ガスの線速度が増大する。

【0014】このように排ガス入り側と排ガス出側とで断面積を異ならせるには、触媒を入りガス側から徐々に連続的に断面積が小さくなるテーパ形状としてもよいし、段階的に断面積が小さくなるようにすることもできる。また一つの触媒でこのような形状としてもよいし、径の異なる複数の触媒を連結してこのような形状とすることもできる。

【0015】また、排ガス入り側の排ガスの線速度より排ガス出側の排ガスの線速度を大きくする手段としては、遠心力など他の力を援用して機械的に排ガス出側の線速度を入り側より大きくすることもできる。しかし装置が大がかりなものとなってスペース面やコスト面で不具合が生じるので、上記のように触媒の断面積を異ならせる手段が特に望ましい。

【0016】排ガス入り側に対し排ガス出側の断面積を小さくする手段を採用する場合には、 $\{100 \times (\text{入り側断面積} - \text{出側断面積}) / \text{入り側断面積}\}$ で表される断面積減少率を20～50%とすることが望ましい。断面積減少率が20%より低いと線速度の増加率が25%以下となり、形状をこのようにした効果が小さく、排ガスの高温域においてSO₂の酸化が生じサルフェートの生成を抑制することが困難となる。また断面積減少率が50%より高くなると、排ガス入り側で酸化されずに残ったHC及びSO_Fを排ガス出側で酸化することが困難となり、HC及びSO_Fの浄化率が低下する。

【0017】触媒の種類としては、コーディエライトなどの耐熱性セラミックスあるいは金属箔などから形成されたハニカム担体基材にアルミナなどの担持層を形成し、それに白金、ロジウム、パラジウムなどの触媒貴金属を担持したハニカム触媒、あるいはアルミナなどのペレットに触媒貴金属を担持したペレット触媒が例示される。

【0018】排ガス入り側と排ガス出側で断面積を異ならせるには、ハニカム触媒の場合にはハニカム担体基材の形状をそのように形成すればよいし、ペレット触媒の場合にはそのような形状のケースにペレット触媒を充填すればよい。

【0019】

【実施例】以下、実施例及び比較例により本発明を具体的に説明する。

（実施例1）図1に本実施例の排ガス浄化用触媒を示す。この触媒は円錐台形状をなし、軸方向に延びる多数のハニカム通路1を有している。そして、排ガス入り側の端面2の直径が117mm、排ガス出側の端面3の直径が82mmとなっている。

【0020】以下、この触媒の製造方法を説明して、構成の詳細な説明に代える。まず押出成形により、コーディエライトから円柱状のハニカム体を形成した。そして乾燥前にハニカム体をプレス成形して円錐台形状とし、それを乾燥焼成して一端面の直径が117mm、他端面の直径が82mm、長さが122mm、容積898ccの円錐台形状のハニカム担体基材を形成した。

【0021】次に、 α -アルミナにアルミナゾルを混合したスラリーを用意し、ハニカム担体基材を浸漬後引き上げて余分なスラリーを拭き払い、120℃で60時間乾燥後500℃で1時間焼成して、アルミナコート層を形成した。アルミナコート層のコート量は、ハニカム担体基材1リットルあたり100gである。さらに、アルミナコート層をもつハニカム担体基材を所定濃度のジニトロジアンミン白金水溶液中に浸漬し、引き上げて余分な水滴を吹き払った後、250℃で1時間熱処理して白金を担持して本実施例の触媒とした。白金の担持量は、ハニカム担体基材1リットルあたり2gである。

【0022】この触媒を直径117mmの大きい方の端面が排ガス入り側端面となるように2.6Lのディーゼルエンジンの排気系に装着し、エンジンベンチでの評価を行った。評価は、エンジン回転数2000rpmにて触媒に500℃の排ガスを1時間流通させた後、排ガスの温度を下げ、400℃、300℃及び200℃においてHCの浄化率とSO₂の転化率を測定した。各温度における測定は、それぞれ10分間かかってその温度まで低下させ、さらにその温度で1時間保持した後に測定した。結果を図3に示す。なおSO₂転化率とは、入りガスに対して触媒上で減少したSO₂の割合をいい、サルフェートの生成量に相当する。

【0023】(実施例2) 図2に本実施例の触媒を示す。この触媒は、直径117mm、長さ61mmの円柱状の第1ハニカム触媒4と、直径82mm、長さ61mmの円柱状の第2ハニカム触媒5からなり、第1ハニカム触媒4と第2ハニカム触媒5とはステンレス製のケース6内に直列に配置されている。なお第1ハニカム触媒4と第2ハニカム触媒5は、それぞれ実施例1の触媒と同様に製造された。

【0024】この触媒を第1ハニカム触媒4側が排ガス入り側となるように2.6Lのディーゼルエンジンの排気系に装着し、実施例1と同様にしてHCの浄化率とSO₂の転化率を測定した。結果を図3及び図4に示す。

(実施例3) 本実施例の触媒は、直径111mm、長さ61mmの第2ハニカム触媒5を用いたこと以外は実施例2と同様である。この触媒についても実施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図4に示す。

【0025】(実施例4) 本実施例の触媒は、直径105mm、長さ61mmの第2ハニカム触媒5を用いたこと以外は実施例2と同様である。この触媒についても実施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図4に示す。

(実施例5) 本実施例の触媒は、直径74mm、長さ61mmの第2ハニカム触媒5を用いたこと以外は実施例2と同様である。この触媒についても実施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図4に示す。

【0026】(実施例6) 本実施例の触媒は、直径95mm、長さ61mmの第2ハニカム触媒5を用いたこと以外は実施例2と同様である。この触媒についても実施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図4に示す。

(比較例1) 直径117mm、長さ122mmの円柱状のハニカム担体基材を用い、実施例1と同様にしてハニカム触媒を形成した。この触媒についても実施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図3及び図4に示す。

【0027】(比較例2) 直径82mm、長さ122mmの円柱状のハニカム担体基材を用い、実施例1と同様にしてハニカム触媒を形成した。この触媒についても実

施例1と同様にしてHCの浄化率とSO₂の転化率を測定し、結果を図3に示す。

(評価) 図3より、比較例1の触媒は特に高温域におけるSO₂転化率が他より高いが、これは排ガス入り側から排ガス出側まで排ガスの線速度が小さいために、特にHC濃度の少ない排ガス出側でSO₂の酸化が生じたためである。また比較例2の触媒は特に低温域におけるHC浄化率が他より低い、これは排ガス入り側から排ガス出側まで排ガスの線速度が大きいために、酸化されなかったHCが排出されたためである。

【0028】一方、実施例1及び実施例2の触媒は、比較例1及び比較例2に比べて高いHC浄化率と低いSO₂転化率を示している。これは排ガス入り側の断面積を大きくするとともに、排ガス出側の断面積を小さくした効果であることが明らかである。また図4から、各触媒の300℃におけるHC浄化率とSO₂転化率を読み取り、それを各触媒の断面積減少率で整理した結果を図5に示す。

【0029】図5より、断面積減少率が20%より低いとSO₂転化率が増大し、50%より高くなるとHC浄化率が減少することがわかる。したがって断面積減少率は、20~50%の範囲が望ましいことが明らかである。

【図面の簡単な説明】

【図1】 本発明の一実施例の排ガス浄化用触媒の斜視図である。

【図2】 本発明の第2の実施例の排ガス浄化用触媒の断面図である。

【図3】 入りガス温度とHC浄化率及びSO₂転化率との関係を示すグラフである。

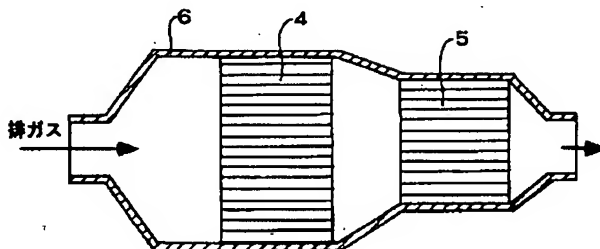
【図4】 入りガス温度とHC浄化率及びSO₂転化率との関係を示すグラフである。

【図5】 断面積減少率とHC浄化率及びSO₂転化率との関係を示すグラフである。

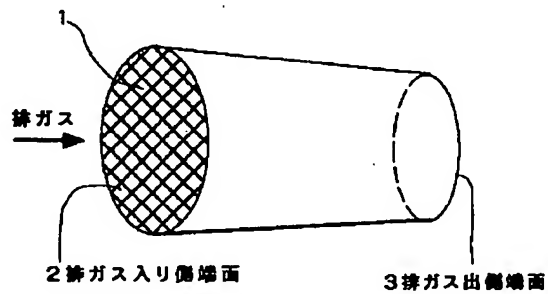
【符号の説明】

1: ハニカム通路 2: 排ガス入り側端面 3: 排ガス出側端面
4: 第1ハニカム触媒 5: 第2ハニカム触媒 6: ケース

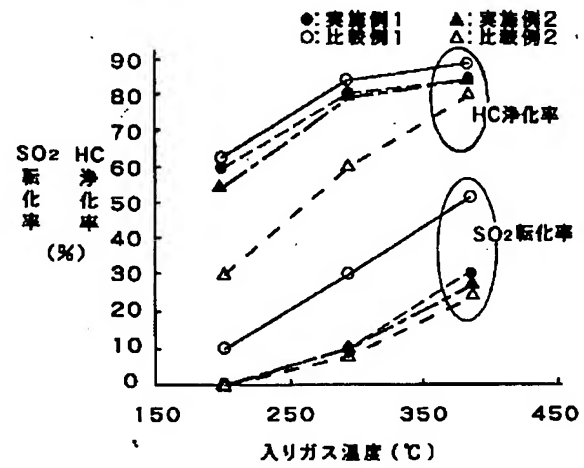
【図2】



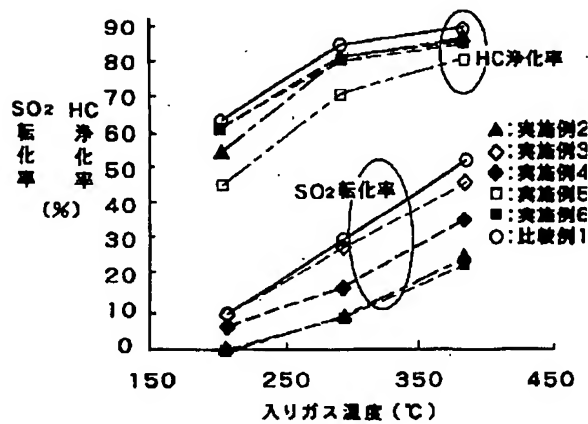
【図1】



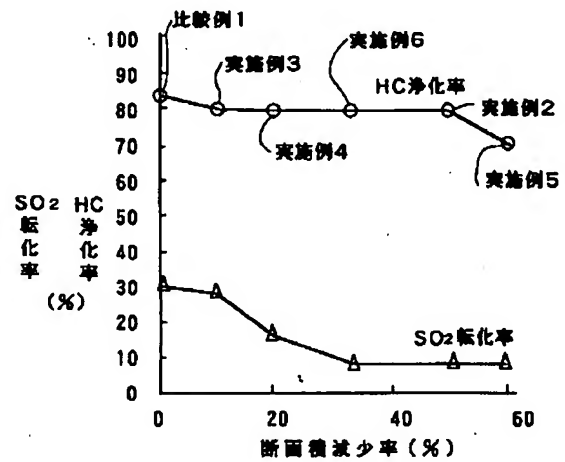
【図3】



【図4】



【図5】



フロントページの続き

(51)Int.Cl.⁶

B01J 35/04

識別記号

ZAB

301

FI

B01D 53/36

ZABD

103C